California Environmental Protection Agency
AIR RESOURCES BOARD

Monitoring and Laboratory Division
Air Quality Surveillance Branch

Sampling Protocol for Diazinon and Propyzamide Ambient Study

July 7, 2009

Prepared by:

Steve Rider
Air Pollution Specialist
Special Purpose Monitoring Section

Signatures:

Kenneth R. Stroud, Chief Date
Air Quality Surveillance Branch
Air Resources Board

Cindy Castronovo, Chief Date
Northern Laboratory Branch
Air Resources Board

The following protocol has been reviewed and approved by staff of the Air Resources Board (ARB). Approval of this protocol does not necessarily reflect the views and policies of the ARB, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

Table of Contents

Section **Page**

Tables

Figures

Appendix

1.0 Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) will conduct ambient air monitoring for the pesticides Diazinon and Propyzamide in Monterey, San Benito and Santa Clara Counties. Ambient Air monitoring for these pesticides will occur over a period of eight weeks. This monitoring will be performed under the requirements of the California Code of Regulation, Food and Agriculture Code, Section 14022(c) which requires the ARB, "…to document the level of airborne emissions…of pesticides that may be determined to pose a present or potential hazard...", when requested by the DPR. Monitoring is being conducted to coincide with the use of Diazinon as an insecticide on lettuce and other food crops for human consumption and Propyzamide as an herbicide used primarily for controlling grasses and some broad-leafed weeds.

The "Standard Operating Procedure Sampling and Analysis of Diazinon" dated June 2009 and "Standard Operating Procedure Sampling and Analysis of Propyzamide" dated June 2009 are included as Appendix A.

2.0 Chemical Properties of Diazinon and Propyzamide

Diazinon: The following information on the physico-chemical properties of Diazinon (see Table 1) are obtained from DPR's, "Use Information and Air Monitoring Recommendations for the Pesticide Active Ingredient Diazinon", dated May 2009 and is included as Appendix B or from the http://extoxnet.orst.edu/pips/diazinon.html website. Diazinon is a nonsystemic organophosphate insecticide and is moderately toxic to humans, birds and laboratory animals. Its principle toxic effect is the inhibition of acetylcholinesterase (AchE). The inhibition of AchE can lead to central nervous system and neuromuscular dysfunction, but its toxic effects are reversible and tend to dissipate after exposure ceases. Diazinon is available in dust, granules, seed dressings, wettable powder and emulsifiable solution formulations. It is generally used on farms to control sucking and leaf eating insects.

Propyzamide: The following information on the physico-chemical properties of Propyzamide (see Table 2) are obtained from DPR's, "Use Information and Air Monitoring Recommendations for the Pesticide Active Ingredient Propyzamide", dated April 2009 and is included as Appendix B or from the http://extoxnet.orst.edu/pips/diazinon.html website. Propyzamide is a white or off-white crystalline solid with no odor. It is relatively stable and is noncorrosive. Propyzamide is practically non-toxic to birds, mammals and warm water fish. It is slightly toxic to cold water fish.

TABLE 1: PHYSICO-CHEMICAL PROPERTIES OF DIAZINON

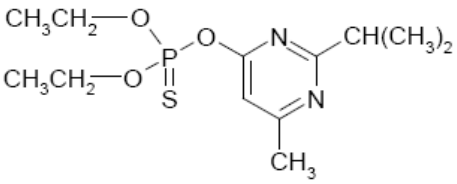
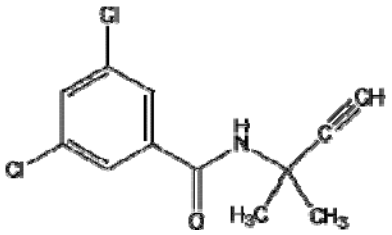
Property	Information
Chemical Name	O,O-Diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate
Chemical Formula	$C_{12}H_{21}N_2O_3PS$
Chemical Structure	
Molecular Weight	304.35
CAS Registry	333-41-5
Color	Colorless
Physical State	Liquid
Odor	Faint ester-like odor
Solubility	40 mg/l @ 20° C
Vapor Pressure	$9.01X10^{-5}$ mm Hg @ 20° C $1.1X10^{-3}$ mm Hg @ 40° C
Henry's Law Constant	$1.17\ X10^{-7}$ atm-m^3/mol
Data Source	Agency for Toxic Substances and Disease Registry (ATSDR, 2008)

TABLE 2: PHYSICO-CHEMICAL PROPERTIES OF PROPYZAMIDE

Property	Information
Chemical Name	3,5-dichloro-*N*-(1,1-dimethyl-2-propynyl)benzamide
Chemical Formula	$C_{12}H_{11}Cl_2NO$
Chemical Structure	
Molecular Weight	256.1
CAS Registry	23950-58-5
Color	Colorless
Physical State	Powder
Odor	Odorless
Solubility	15 mg/L (ppm) (at 25 °C)
Vapor Pressure	0.058 mPa (at 25 °C) 8.5 x 10^{-5} mmHg (at 25 °C)
Henry's Law Constant	9.8 x 10-9 (at 25 °C)
Data Source	CDPR, BCPC 2000 and Extoxnet

3.0 Project Goals and Objectives

The goal of this monitoring project is to measure the concentrations of both Diazinon and Propyzamide in ambient air throughout Monterey, San Benito and Santa Clara Counties.

To achieve the project goals, the following objectives should be met:

1. Identification of monitoring sites that mutually satisfies criteria for ambient air sampling and DPR's requirements.

2. Appropriate application of sampling/monitoring equipment to determine ambient Diazinon and Propyzamide concentrations.

3. Application of relevant field quality assurance/quality control practices to ensure the integrity of field samples.

4. At the conclusion of the project, MLD will provide DPR with a final report containing all relevant information, data and execution of this project.

4.0 Contacts

Mac McDougall, Manager
Special Purpose Monitoring Section
916-327-4720
emcdouga@arb.ca.gov

Steve Rider, Air Pollution Specialist
Special Purpose Monitoring Section
Office 916-327-4719 Cell 916-718-2488
srider@arb.ca.gov

Jack Romans, Air Pollution Specialist
Special Purpose Monitoring Section
Office 916-327-4716 Cell 916-952-9520
jromans@arb.ca.gov

Russell Grace, Manager
Special Analysis Section
Office 322-2496
rgrace@arb.ca.gov

Pam Wofford, Senior Environmental Scientist
Department of Pesticide Regulation
916-324-4297
pwofford@cdpr.ca.gov

5.0 Study Location and Design

Diazinon and Propyzamide are used throughout the State of California and throughout the calendar year. 2007 data shows that Monterey County has the highest Diazinon and Propyzamide use by a factor of three (3) over the second highest use counties of Fresno (Diazinon) and Santa Barbara (Propyzamide). In Monterey County, use of both pesticides is highest during the months of June through August. Propyzamide usage drops off tremendously in the month of September. DPR has requested that ARB perform ambient air monitoring for Diazinon and Propyzamide during the summer months.

Ambient Air Monitoring

The sampling process is designed to collect both Diazinon and Propyzamide on a single XAD resin sorbent tube. The Laboratory will extract both pesticides from each sample tube for analysis.

Samples will be collected by passing a measured volume of ambient air through one XAD resin sorbent tube that is mounted on a sampling tree as shown in Figure 1. The exposed XAD-2 resin sorbent tubes (SKC #226-30-06) with 400 and 200 mg of packing are stored in an ice chest (on dry ice) or in a freezer until extracted in the laboratory with organic solvent. The sampling flow rates of 3.0 liters per minute (LPM) for both pesticides will be accurately measured and the sampling system operated continuously

for 24 hours ± 1 with the exact operating interval recorded on the log sheet. The resin sorbent tubes will be protected from direct sunlight or rain and supported about 1.7 meters above the ground or roofline. Whether on the ground or a rooftop there shall not be any major obstructions and each site must meet generally accepted siting criteria for the ambient monitoring. At the end of each sampling period, the tubes will be placed in culture tubes with an identification label affixed. At least once a week, collected samples will be transported on dry ice to ARB's Monitoring and Laboratory Division laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately.

Sample flow is controlled by an inline rotameter (flow range of 0-5 LPM). Each site will have one (1) collocated sample per week. Prior to each sampling period, the sampler is leak checked with an unopened sacrificial resin sorbent tube. After the sample resin sorbent tube is installed, the flow rate is set at 3.0 LPM using a digital mass flow meter. The flow rate will be checked at the end of each sampling period, the start/end flows are documented on the log sheet and resin sorbent tube label. The end flow must be within ± 20% of 3.0 LPM (± 0.6 LPM or 2.4–3.6 LPM). The field log sheet (see Figure 2) and resin sorbent tube label will contain the following information: log #, sample name, sampler ID number, start and end date and time, start and end counter reading, start and end mass flow meter display reading, comments (if applicable), weather conditions and the start and end initials of the operator.

FIGURE 1: AIR SAMPLER TREE WITH PUMP

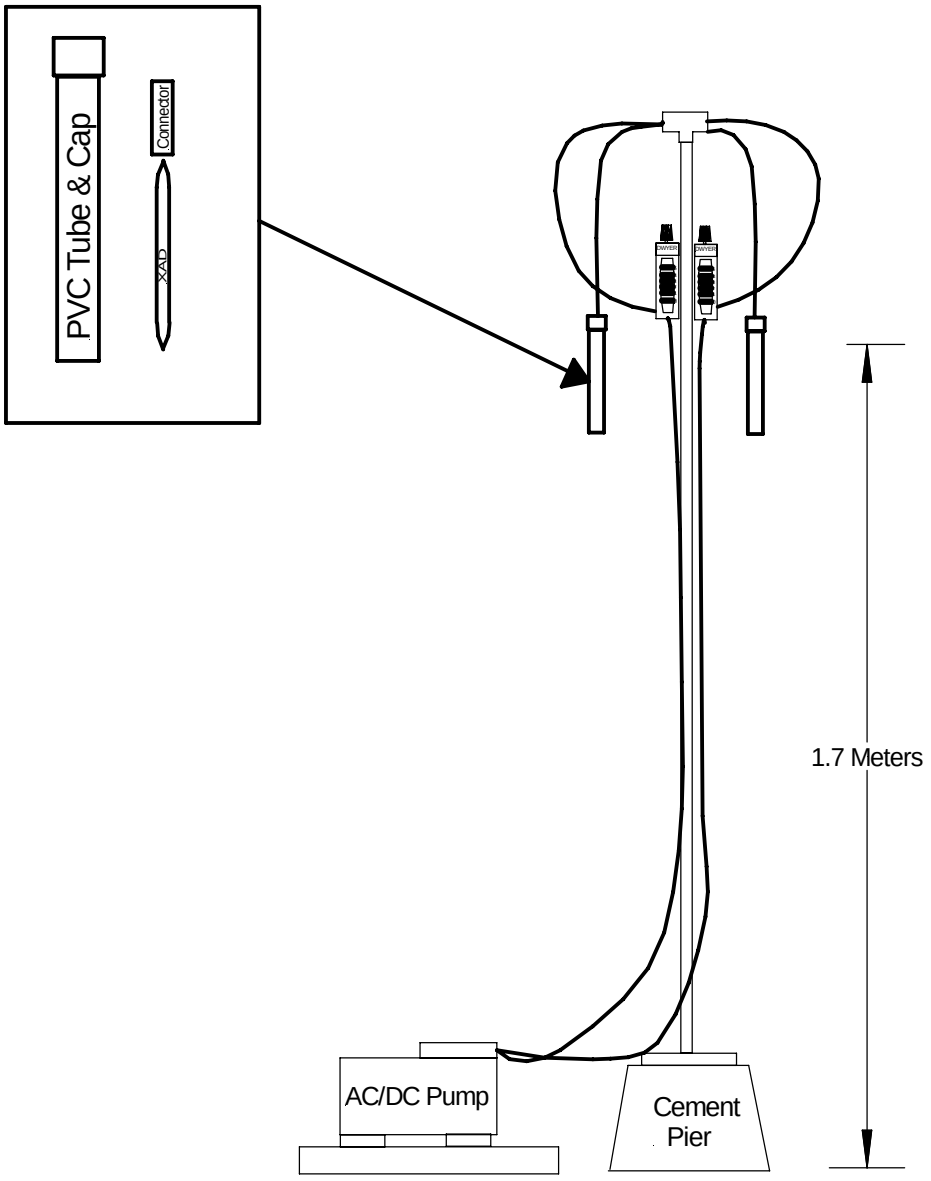


FIGURE 2: FIELD LOG SHEET
RESIN SORBENT TUBE FIELD LOG SHEET

Project: Diazinon and Propyzamide Pesticide Ambient Air Monitoring

Start Flow Set: 3.0 ±0.1 lpm End Flow Criteria: 3.0 lpm ±20%

Log #	Sample Name	Sampler ID Number	Date & Time Entry Example (6/14/08 13:42)		Counter		Mass Flow Meter Display		Corrected Average Flow	Comment Number	Weather K,P,C,F&R		Initials	
			Start	End	Start	End	Start	End			Start	End	Start	End

MFM Used #: _____ **Slope:** _____ **Intercept:** _____

1 of 12

Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog and R = Rain (any)

Six sampling sites (five air monitoring sites and one urban background site) were selected in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations or other public buildings). Each air monitoring site is located in proximity to fields which have Diazinon and Propyzamide applied. Pesticide air monitoring site locations are determined using historical pesticide use information supplied by the California Department of Pesticide Regulation's 2009 monitoring recommendations. Sites are located in areas with historically high Diazinon and Propyzamide pesticide use.

The ambient monitoring sites in Monterey and San Benito Counties are located at:

Gilroy – Background Site
Gilroy Monitoring Station – Bay Area AQMD
Located at Glen View Elementary School
695 9th Street
Gilroy, CA

Hollister
R.O Hardin K-5 School
761 South Street
Hollister, CA

Salinas
Santa Rita School District – Maintenance Facility
56 Rogge Road
Salinas, CA

Chualar
Salinas Rural Fire District – Chualar Station
24281 Washington Street
Chualar, CA

Soledad
Jack Franscioni Elementary School
779 Orchard Lane
Soledad, CA

King City
King City Monitoring Station – Monterey Bay Unified APCD
Located at San Lorenzo Elementary School
421 Pearl Street
King City, CA

Sampling schedules during this ambient monitoring project will reflect current furlough and overtime policies. ARB staff will continue to collect samples for an eight (8) week period (July – August '09). As agreed by the Department of Pesticide Regulations, alterations to the propyzamide recommendation will result in three (3) 23-hour samplers per week. Sampling will begin at the first site on Monday morning at approximately 11:00 am. Samples will be removed and new sample media installed 23 hours later on

Tuesday morning, and again 23 hours later on Wednesday morning. The third set of samples will be removed 23 hours later at approximately 8:00 on Thursday morning. All flow rates will be set to 3.0 LPM.

6.0 Sampling and Analysis Procedures

Special Purpose Monitoring Section (SPM) personnel will hand-carry samples to and from MLD's laboratory in Sacramento, and to and from the sampling location. The samples will not be exposed to extreme conditions or subjected to rough handling that might affect sample integrity.

At each sampling site, the operator will assure that all required sample collection information is recorded on the affixed XAD resin sorbent tube identification label and field log sheet. After removing samples from the sampling tree, samples are placed in a glass tube and stored in a cooler with dry ice at 4° C or less until returned to the laboratory. The sample tubes will be transported as soon as reasonably possible to ARB's Sacramento Monitoring and Laboratory Division laboratory for analysis. These samples will be stored in the freezer or extracted/analyzed immediately. Samples are collected in the field with a flow rate of 3.0 LPM.

All reported sampling times will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch (NLB) will supply SPM with XAD resin sorbent tubes and will perform analyses for Diazinon and Propyzamide on the collected ambient samples and report results to SPM.

Laboratory analyses will be performed in accordance with applicable standard operating procedures (Standard Operating Procedure Sampling and Analysis of (Diazinon) and (Propyzamide)) included as Appendix A.

The XAD resin sorbent tube sample validation and analytical quality control criteria are as follows.

1. **Sample Hold Time**: Sample hold time criteria will be established by the Laboratory. Samples not analyzed within the established holding time will be invalidated by the Laboratory.

2. **Replicate Analysis**: Laboratory to establish relative percent difference (RPD) criteria for replicate analysis. Replicate analysis shall be performed on every tenth sample (10%) per analytical batch sequence (excluding standards, controls and other quality control data). Lab to provide replicate analytical results and RPD.

3. **Method Detection Limit (MDL)**: Sample analytical results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions/concentrations.

4. **Analytical Linear Range**: Any analytical result greater than the highest calibration standard shall be reanalyzed within the calibrated linear range.

7.0 List of Field Equipment

Quantity	Item Description
(7)	Pesticide stick samplers with 2 ea. rotameters and separate plumbing for use with two (2) pumps
(7)	Cement piers for holding pesticide stick samplers
(13)	AC pumps
(1)	Global Positioning System (GPS) with backup batteries and carrying case
(1)	Digital Camera with backup batteries and carrying case
(2)	Aalborg mass flow meter 0-5 LPM.
(1)	Dry ice chest
(1)	Ladder
(7)	Extension cords
(7)	Elapsed time meters

8.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. National Institute of Standards and Technology (NIST)-traceable transfer standards will be used to measure sample flow rates.

The sample flow rate of the passive flow controllers will be measured using mass flow meters having a current calibration certification and a range of 0-5 liters per minute (LPM).

Each XAD resin sorbent tube will be assigned a field sample number that provides for identification of site, sample ID number, operator, and sample information as well as sample transfer information.

Field Spike (FS): A field spike will be prepared by the laboratory by injecting a resin sorbent tube with 72 nanograms (ng) of Diazinon, 130 ng of Diazoxon and 1 microgram (ug) of Propyzamide. The field spike is installed onto a sampler and will be collocated with the primary sampler. There will be a minimum of four (4) field spikes throughout the study.

Trip Spike (TS): A trip spike will be prepared by the laboratory by injecting a XAD resin sorbent tube at the same level as the field spike. The trip spike will be transported and analyzed along with the field spike. The trip spike is treated the same as a field spike with exception that it is not installed onto a sampler.

Trip Blank (TB): Field Staff will prepare one trip blank per week of sampling. The trip blank resin sorbent tube accompanies the sample resin sorbent tubes from the lab to the field and returns but is not installed onto a sampler.

Collocated (CO): For ambient monitoring, collocated (side-by-side) air samplers will operate once per week at each site for all eight (8) weeks of the monitoring period.

Site/Sample Identification

The Diazinon/Propyzamide sampling sites will be named accordingly for the locations, run and type of sample:

Ambient Site Naming:

GIL1-24 Gilroy ARB site Weeks 1 through 8
HOL1-24 Hollister site Weeks 1 through 8
SAL1-24 Salinas site Weeks 1 through 8
CHU1-24 Chualar site Weeks 1 through 8
SOL 1-24 Soledad site Weeks 1 through 8
GRE1-24 Greenfield site Weeks 1 through 8

Letter Abbreviations as follows
FS = Field Spike
C = Collocated
TS = Trip Spike
TB = Trip Blank

Examples: SAL5 = Salinas run #5.
SAL5-C = Salinas, run #5 and it is a collocated sample.

Each sample will be assigned a unique and sequential log number.

Following the quality control procedures listed above will insure the quality and integrity of the samples collected in the field and will insure accurate field and lab data collection.

9.0 Deliverables

9.1 Air Quality Surveillance Branch Deliverables

Within 60 days from receipt of the final results report from the Northern Laboratory Branch (NLB), AQSB will provide DPR with a draft report for review containing the following topics:

1) Sampling Protocol.
2) Personnel Contact List.
3) Site Maps.
4) Site Photographs.
5) Site Descriptions and Measurements, GPS coordinates, inlet height.
6) A map of the monitoring site locations.
7) Sample Summary Table.
8) Field Sample Log.
9) Laboratory Analysis Reports with calculations in electronic format.
10) Transfer Standards' Certification Reports.
11) Disk containing electronic files of Report.

In addition, the Special Purpose Monitoring Section (SPM) will prepare a project binder containing the above information. This binder will remain with SPM though available for viewing and review as requested.

9.2 Northern Laboratory Branch (NLB) Deliverables

Within 60 days from the last day of analysis, The NLB will provide SPM with a report that will include the following topics:

1) Analytical result table(s) to include:
    a. Sample identification (name).
    b. Date sample received from field.
    c. Date sample analyzed.
    d. Dilution ratio.
    e. Analytical results.
    f. Quality control results.
2) All equations used in calculating analytical results.
3) Table of duplicate/replicate results including calculated relative percent difference (RPD).
4) Table of collocated results including calculated relative percent difference (RPD).
5) Table of analytical results from all field spikes.
6) Table of analytical results from all trip and laboratory spikes including percent recoveries.
7) Table of analytical results from all trip blanks.
8) Table of analytical results from all laboratory blanks, standards and control checks performed, including dates performed and relative percent recoveries if applicable.
9) Copy or location of analytical method or Standard Operating Procedures (SOP) used for analysis.
10) Section or provision listing or reporting any and all deviations from analytical SOP and this protocol.

APPENDIX A: Standard Operating Procedure Analyses for Diazinon and Propyzamide

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for Diazinon collected by the XAD resin sorbent tube method. This analytical procedure is entitled, Standard Operating Procedure Sampling and Analysis of (Diazinon).

The Special Analysis Laboratory Section of MLD's Northern Laboratory Branch will perform the analyses for Propyzamide collected by the XAD resin sorbent tube method. This analytical procedure is entitled, Standard Operating Procedure Sampling and Analysis of (Propyzamide).

California Environmental Protection Agency

Air Resources Board

Standard Operating Procedure
Sampling and Analysis of O,O-diethyl O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate (Diazinon) and the Oxygen analog (Diazoxon)

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

June 2009

Version 1

Approved by:

Russell Grace, Manager
Special Analysis Section

1. SCOPE

This is a gas chromatography/mass spectrometer (GC/MS) method for the determination of O,O-diethyl- O-2-isopropyl-6-methylpyrimidin-4-yl phosphorothioate (Diazinon) and the oxygen analog (Diazoxon) from ambient air samples.

2. SUMMARY OF METHOD

Ambient air samples are collected on XAD-2 sorbent tubes. Sampled tubes are stored at four degrees centigrade (4°C) or lower prior to extraction. Sample tubes are extracted using pesticide grade ethyl acetate (EtAc). Sample analysis is performed using a gas chromatograph with a mass spectrometer (GC/MS) in the selected ion-monitoring mode (SIM). Sample analysis and quantitation uses an internal standard method for instrument calibration. Estimated quantitation level (EQL) for this method is approximately 0.013 microgram per cubic meter ($\mu g/m^3$) prior to any sample dilution.

3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in solvents, reagents, glassware and the XAD-2 tubes that can lead to discrete artifacts or elevated baselines. Analysis of samples containing high concentrations of early eluting components may cause significant contamination of the analytical equipment. Both a system blank and method blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

4. EQUIPMENT AND CONDITIONS

a) Instrumentation

Hewlett Packard 6890 Series Plus gas chromatograph:
Column: Rtx CLPesticide, 30 meter, 0.32mm I.D., 0.50 micron film thickness.
GC temperature program: initial 100^o C, initial time 2 minutes, to 250^o C @ 50^o C/min, hold 5 minutes.
Carrier Gas: Helium, grade 5.
Inlet set to pulsed splitless mode: 50 psi for 1 minute opened at 1.25 Minutes.

Hewlett Packard 5973N mass selective detector:
Acquisition Mode: SIM.
Tune File: PFTBA Autotune.
Ions Monitored: 183, 199, 273, 288, 304, 314.
Quant Ions: 304, 273.
Internal standard ion: 314.

Solvent Delay: 5.00 min.

b) Auxiliary Apparatus

XAD-2 tubes (400/200 mg) (SKC cat # 226-30-6) or equivalent.
Glass amber vials, 2-ml capacity with Teflon septum caps.
Glass vials, 8-ml capacity with Teflon septum caps.

c) Reagents

Ethyl Acetate(EtAc) (B&J brand Pesticide grade or equivalent).
Dichloromethane.
Diazinon 99.4% pure (Chem Service Inc. PS-90).
Diazinon-O analog solution 99.9 µg/ml (Accustandard P-640S-A).
Diazinon-(diethyl-d-10) solution 100µg/ml (Chem Service Inc. FD2060S).

d) Gases

Compressed helium grade 5.

5. SAMPLE COLLECTION

a) Samples are collected in the field with a maximum flow rate of three (3) liters per minute (lpm).
b) After collection the samples are place in a glass tube and stored in a cooler at 4° C or less until returned to the laboratory.
c) Diazinon and Diazoxon are stable for up to 28 days when kept at -20°C. **See Appendix 1 section 8F in the Method Development Report for the storage stability summary.**

6. SAMPLE EXTRACTON

a) Prepare a method blank and laboratory control sample (LCS) tube with every batch of field samples not to exceed twenty (20) samples in an analytical batch.
b) Spike the LCS with 72/130 ng of diazinon/diazoxon before extraction.
c) Carefully score and break the sample XAD-2 tube just above the glass wool plug on the primary section.
d) Remove the glass wool plug using forceps. Pour the XAD-2 resin from the primary section into an 8 ml glass vial.
e) Retain the secondary section for later analysis to check for sample breakthrough.
f) Using three (3.0) ml of EtAc carefully rinse the inside of the primary section into the glass vial.

g) Add 30 µl of a 10µg/ml diazinon-d-10 internal standard to the glass vial. Cap tightly.

h) Allow XAD-2 to sit for approximately one hour with occasional swirling of XAD-2 in the solvent.

i) After extraction the samples are ready for analysis or if not to be analyzed immediately the samples should be stored in a refrigerator at 4º C.

7. ANALYSIS OF SAMPLES

a) Transfer approximately 0.25 ml of the sample extract into a 1.5-ml autosampler vial equipped with a 0.25 ml insert. Sample extract is now ready for analysis.

b) A 2-µl injection volume will be used for all analyses.

c) Perform an initial calibration curve using concentrations at or near the EQL to approximately 30 times higher. At least five (5) points must be analyzed to establish a calibration curve. Calibration curve acceptance requires an r^2 of at least 0.995. Appendix 2 lists the standard concentrations used when the EQL is approximately 0.013 µg/m^3.

d) Prepare a sample sequence for the GC/MSD. The sequence should include a system blank, and a continuing calibration verification standard (CCV), for every ten (10) samples analyzed. The CCV should be made from a lot number that differs from the lot number used to make the calibration curve. If a differing lot number is not available the CCV should be made up independently from the calibration curve.

e) If this batch of samples includes a method blank and /or LCS, they should be run prior to field samples to verify that QC criteria have been met.

f) Because of the nature of the XAD-2 tube, extraneous components will be extracted along with the analytes of interest. To minimize excessive carry over of these contaminants from one analysis to the next, a system blank should be run after every ten (10) to twenty (20) samples or more frequently if indicated by sample chromatograms. In no case should a sample contaminant interfere with the peaks of interest. This will be verified by the absence of a peak in the analyte retention time window during the system blank analysis.

g) Review and edit the quantitation reports as needed.

h) The samples must be diluted if the analytical results are not within the calibration curve. Every attempt should be made to have the diluted results fall within the upper half of the calibration curve.

i) If a sample needs dilution then additional internal standard will be added to bring the final concentration back to 100ng/ml

j) The final results will be adjusted by an appropriate dilution factor and reported in ng/ml.

k) The atmospheric concentration is calculated according to:

$$\text{Ambient Sample Conc. (ng/m}^3\text{)} = \frac{\text{Extract Conc. (ng/ml) x 3 ml}}{\text{Air Volume Sampled (m}^3\text{)}}$$

l) Given instrument sensitivity and a maximum sample volume of 4.32 m^3 the EQL for this method will be approximately 13.0 ng/m^3 (0.013µg/m^3).

8. QUALITY ASSURANCE

a) A system blank must be analyzed with each batch of samples. The system blank is an aliquot of the solvent used to extract the samples. The analyte concentration must be below the method detection limit (MDL) established for the method. A system blank is run at the beginning of the analytical batch, and after the calibration curve or CCV just prior to sample analysis.

b) A minimum of a five point calibration curve will be run at the beginning of each project and whenever major instrument maintenance of repair is performed, and whenever the CCV exceeds the acceptable variation.

c) A CCV will be run at the start of each analytical batch and after every tenth sample to verify the system linearity. The CCV quantitated value must be within 25% of the actual value.

d) A method blank will be run with each batch of 20 or fewer samples. The method blank is a blank XAD-2 tube that is run through the entire method. The analyte concentration must be below the MDL established for the method.

e) A LCS will be run with every batch of 20 or fewer samples. The LCS analyte concentrations should fall within the lower half of the calibration curve. Using the calibration curve exhibited in Appendix 2, the spike level should be approximately 24/43 ng/ml. The LCS should be made from a lot number that differs from the lot number used to make the calibration curve. If a differing lot number is not available the LCS should be made up independently from the calibration curve. The analytical value of the LCS must be within three standard deviations of its historical mean. If the LCS is outside these limits then the samples in the analytical batch must be reanalyzed.

f) Run other project specific quality control samples, such as lab spikes, trip spikes, and field spikes prior to field samples. A system blank should be run after the spiked samples to ensure that spiked analyte does not carry over into the field samples.

9. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

Appendix 2

Calibration Standard Preparation for Diazinon/Diazoxon

The certified neat standard used for diazinon calibration was purchased from Chem Service Inc., West Chester, Pennsylvania and has the following specification:

Lot No:	409-19B
Expiration date:	July 2011
Diazinon:	99.4% pure (solid)

The certified neat standard used for diazoxon calibration was purchased from AccuStandard, Inc., New Haven, Connecticut and has the following specification:

Lot No:	B9010227
Expiration date:	January 2011
Diazoxon:	99.9 µg/ml solution

A stock standard with a concentration of approximately 1 to 5 milligram (mg) per ml was prepared by weighing 25 to 125 mg of Diazinon into a 25 ml volumetric flask and bringing to volume with methylene chloride. The Diazoxon was diluted from the premade standard solution of 99.9 µg.ml.

Using a serial dilution technique the following calibration standards were prepared in Ethyl Acetate: 11/25, 22/50, 45/100, 90/200, 180/400, 360/800 ng/ml.

A minimum of six standards was used to generate the calibration curve, with the standard at 11/25 ng/ml being the low point. The low point equates to approximately 7.6/17.4 ng/m^3.

All standard and sample injections used a volume of 2.0 µl.

Initial calibration curve acceptance requires an r^2 of at least 0.995.

California Environmental Protection Agency

Air Resources Board

Standard Operating Procedure
Sampling and Analysis of Propyzamide

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

June 2009

Version 1

Approved by:

Russell Grace, Manager
Special Analysis Section

1. SCOPE

This is a gas chromatography/electron capture detector (GC/ECD) method for the determination of propyzamide in ambient and application air sampling.

2. SUMMARY OF METHOD

Ambient and application air samples are collected on XAD-2 sorbent tubes. Sampled tubes are stored at four (4) degrees centigrade (°C) or lower prior to extraction. Sample tubes are extracted using pesticide grade ethyl acetate. Sample analysis is performed using a GC/ECD. Sample analysis and quantitation uses external standard method for instrument calibration. Estimated quantitation level (EQL) for this method is approximately 5.0 micrograms per cubic meter ($\mu g/m^3$) prior to any sample dilution.

3. INTERFERENCES / LIMITATIONS

Method interference may be caused by contaminants in solvents, reagents, glassware and the XAD-2 tubes that can lead to discrete artifacts or elevated baselines. Analysis of samples containing high concentrations of early eluting components may cause significant contamination of the analytical equipment. Both a system blank and method blank must be analyzed with each batch of samples to detect any possible method or instrument interference.

4. EQUIPMENT AND CONDITIONS

A. Instrumentation

- Agilent Technologies 7890 Series gas chromatograph with Agilent Model 7683B injector.
- Column: Agilent HP-5, 30 meter, 0.32mm I.D., 0.25 micron film thickness, with helium as carrier gas at constant flow and nitrogen as the makeup gas at 25 ml/min.
- GC temperature program: initial 100^o C, initial time 2 minutes, to 260^o C @ 12^o C/min, hold 2 minutes.
- Inlet temperature 260^o C; splitless.
- Detector temperature 325^o C.

B. Auxiliary Apparatus

- XAD-2 tubes (400/200 mg) (SKC cat # 226-30-6) or equivalent
- Glass amber vials, 2-ml capacity with septum caps.

C. Reagents

- Ethyl Acetate(EtAc) (B&J brand HPLC grade or equivalent)
- Propyzamide 98.1%, Chem Services PS-349

5. SAMPLE COLLECTION

a) Samples are collected in the field with a maximum flow rate of three (3) liters per minute (lpm).
b) After collection the samples are placed in a glass tube and stored in a cooler at 4° C or less until returned to the laboratory.
c) Samples are stored at 4° C or less until ready for analysis.

6. SAMPLE EXTRACTON

a) Prepare a method blank and laboratory control sample (LCS) tube with every batch of field samples not to exceed twenty (20) samples in an analytical batch. The LCS is spiked with 3 µg of propyzamide before extraction.
b) Carefully score and break the sample XAD-2 tube just in front of the glass wool plug on the primary section.
c) Remove the glass wool plug using forceps. Pour the XAD-2 resin from the primary section into an 8 ml glass vial.
d) Score the tube just in front of the secondary section glass wool. Retain the secondary section for later analysis to check for breakthrough.
e) Using three (3.0) ml of EtAc carefully rinse the inside of the primary section into the glass vial. Cap securely.
f) The extracts are allowed to sit at room temperature for 1 hour. The extracts are ready for analysis or if not analyzed are stored in a refrigerator at 4º C.

7. ANALYSIS OF SAMPLES

a) Transfer approximately 0.25 ml of the sample extract into a 1.5-ml autosampler vial equipped with a 0.25 ml insert. Sample extract is now ready for analysis.
b) A 1-µl injection volume will be used for all analyses.
c) Perform a calibration curve using concentrations at or near the EQL to approximately 10 times higher. At least five (5) points must be analyzed to establish a calibration curve.

d) Prepare a sample sequence for the GC/ECD. The sequence should include a system blank and a calibration control standard, for every ten (10) samples analyzed. If this batch of samples includes a method blank and /or LCS, they should be run prior to field samples to verify that QC criteria have been met.

e) Because of the nature of the XAD-2 tube, extraneous components will be extracted along with the analytes of interest. To minimize excessive carry over of these contaminants from one analysis to the next, a system blank should be run after every ten (10) to twenty (20) samples or more frequently if indicated by sample chromatograms. In no case should a sample contaminant interfere with the peaks of interest. This will be verified by the absence of a peak in the analyte retention time window during the system blank analysis.

f) Review and edit the quantitation reports as needed.

g) The samples must be diluted if the analytical results are not within the calibration curve. Every attempt should be made to have the diluted results fall within the upper half of the calibration curve.

h) The final results will be adjusted by an appropriate dilution factor and reported in µg/ml.

i) The atmospheric concentration is calculated according to:

$$\text{Ambient Sample Conc. } (\mu g/m^3) = \frac{\text{Extract Conc. } (\mu g/ml) \times 3 \text{ ml}}{\text{Air Volume Sampled } (m^3)}$$

j) Given instrument sensitivity and a maximum sample volume of 4.32 m^3 the EQL for this method will be approximately 0.35 $\mu g/m^3$.

8. QUALITY ASSURANCE

a) A system blank must be analyzed with each batch of samples. The system blank is an aliquot of the solvent used to extract the samples. The analyte concentration must be below the method detection limit (MDL) established for the method. A system blank is run at the beginning of the analytical batch, after the calibration curve, or just prior to sample analysis.

b) A minimum five point calibration will be run with each sample batch.

c) A calibration control will be run after the calibration, every tenth sample and at the end of the sample batch to verify system linearity. The calibration control values must be within 25% of the actual value.

d) A method blank will be run with each sample batch. The method blank is a blank solvent that is run through the entire method. The analyte concentration must be below the MDL established for the method.

e) A LCS will be run with every sample batch. The LCS analyte concentration should fall within the lower half of the calibration curve. The

LCS stock standard should come from a different source or lot than the daily calibration standards. If not available then this should be prepared separately from the calibration curve. The analytical value of the LCS must be within three standard deviations of its historical mean. If the LCS is outside these limits then the samples in the analytical batch must be reanalyzed.

f) Run specific quality control samples, such as field spikes, trip spikes, and laboratory spikes prior to the field samples. A system blank should be run after the spiked samples to ensure that spiked analyte does not carry over.

9. Safety

This procedure does not address all of the safety concerns associated with chemical analysis. It is the responsibility of the analyst to establish appropriate safety and health practices. For hazard information and guidance refer to the material safety data sheets (MSDS) of any chemicals used in this procedure.

APPENDIX B:
Use Information and Air Monitoring Recommendations for the Pesticide Active Ingredient Diazinon
and
Use Information and Air Monitoring Recommendations for the Pesticide Active Ingredient Propyzamide

HTTP://WWW.CDPR.CA.GOV/DOCS/EMON/PUBS/TAC/RECOMM/AIR_RPT_DIAZINON.PDF

HTTP://WWW.CDPR.CA.GOV/DOCS/EMON/PUBS/TAC/RECOMM/AIR_RPT_PROPYZAMIDE.PDF